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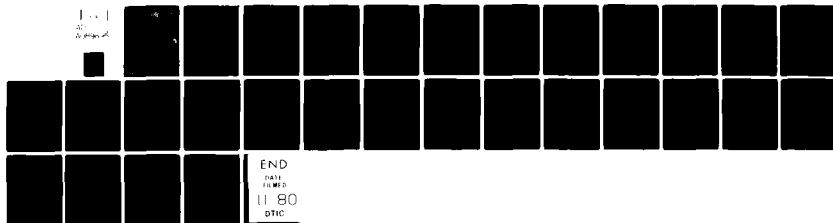
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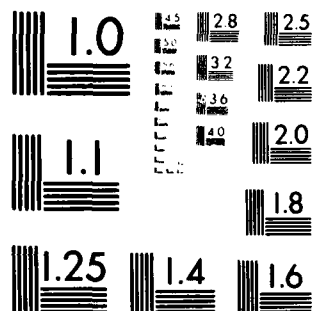
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X-Ray Photoelectron Spectroscopy Study of the Chemisorption of Lead Naphthenate to Nucleophilic Surfaces

P. A. BERTRAND and P. D. FLEISCHAUER
Laboratory Operations
The Aerospace Corporation
El Segundo, Calif. 90245

10 September 1980

Interim Report

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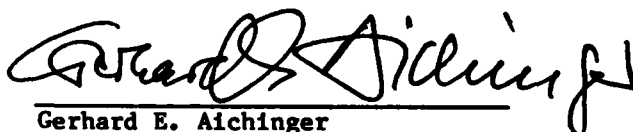
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Prepared for
SPACE DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, Calif. 90009

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This interim report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-79-C-0080 with the Space Division, Contracts Management Office, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by S. Siegel, Director, Chemistry and Physics Laboratory. Gerhard E. Aichinger was the project officer for Mission-Oriented Investigation and Experimentation (MOIE) Programs.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.



Gerhard E. Aichinger
Project Officer

FOR THE COMMANDER



Evan R. Brossman, Chief
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19 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
18 1. REPORT NUMBER SD-TR-80-66	2. GOVT ACCESSION NO. AD-A089895	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF THE CHEMISORPTION OF LEAD NAPHTHENATE TO NUCLEOPHILIC SURFACES.		5. TYPE OF REPORT & PERIOD COVERED 9 Interim Report	
7. AUTHOR(s) 10 Patricia A. Bertrand Paul D. Fleischauer		6. PERFORMING ORG. REPORT NUMBER 14 TR-0080(5970-03)-1	
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Aerospace Corporation El Segundo, CA 90245		8. CONTRACT OR GRANT NUMBER(s) 15 F04701-79-C-0080	
11. CONTROLLING OFFICE NAME AND ADDRESS Space Division Air Force Systems Command Los Angeles, CA 90009		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 12 01	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE 11 10 September 1980	
		13. NUMBER OF PAGES 25	
		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) ESCA Lead Naphthenate Lubrication Photoelectron Spectroscopy (... (7-))			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The adsorption of lead naphthenate on the surfaces of metals, oxides, and sulfides was studied by means of x-ray photoelectron spectroscopy (XPS). Lead naphthenate physically adsorbs on all surfaces. It chemisorbs on surfaces with basic sites, such as oxides, sulfides, and metals treated in basic solutions before adsorption. The two states have distinct XPS spectra: the Pb(4f _{7/2}) binding energy for the physically adsorbed state is 139.1 eV, whereas that			

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19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

for the chemisorbed state is 136.6 eV. Conditions of surface preparation that result in the formation of each state are described.

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INTRODUCTION

There are two general types of molecular adsorption on surfaces. One is physical adsorption, which is characterized by weak bonding forces such as Van der Waals forces; the other is chemisorption, which has a strong chemical interaction between the adsorbed molecule and the surface. A molecule that is chemisorbed to a surface has different properties than a physically adsorbed molecule. The most obvious difference between the two states is that more energy must be put into the molecule-surface system to break a chemisorptive bond (up to 30 kcal/mol) than to remove a physically adsorbed molecule (less than 10 kcal/mol).

Lead naphthenate is a lubricant additive that decreases wear in moving assemblies under boundary lubrication conditions. The binding of this substance to surfaces is important to its function as a boundary lubricant since it must protect the moving parts even when the major component of the lubricant (e.g., the oil) is not present. It is generally agreed that a good boundary lubricant will chemisorb to the surface; in this way, the material will remain where it was applied even under local heating conditions that would cause a physically adsorbed material to move. The question is whether lead naphthenate is physically adsorbed or chemisorbed to the surface.

In this study, x-ray photoelectron spectroscopy (XPS) was used to investigate the bonding of lead naphthenate to surfaces. During the experiments, it was found that both physically adsorbed and chemisorbed lead naphthenate could be present on any given surface. Also, the surface

conditions (e.g., surface composition and acidity), as determined by preparation procedures, played an important role in the type of bonding between the molecule and the surface.

EXPERIMENTAL

The spectra were taken with a GCA/McPherson ESCA-36 x-ray photoelectron spectrometer equipped with an electrostatic analyzer. Control, data acquisition, and readout were directed by a PDP-8E computer with a 24,000-word memory. The sample chamber can be evacuated to a pressure of 10^{-6} Torr in under 15 min, but spectra were generally not taken until the pressure had reached 10^{-7} Torr.

The lead naphthenate was a viscous brown material obtained from Bardahl, lot number 104M. Naphthenes are cyclic-saturated hydrocarbons of the polymethylene type. The simplest naphthenic acid is 1-methylcyclopentane-carboxylic acid. Lead naphthenate is not one unique compound but a mixture of several naphthenates with various alkane chain lengths and an average molecular weight of 662 g/mol. It contains no free naphthenic acid. Solutions of 1% by weight lead naphthenate in heptane were used in these experiments.

The substrates (coupons of Nylon 66, Teflon FEP, Kapton, 304 and 440C steels, copper, and gold) were cleaned in trichloroethylene and in acetic acid and rinsed in water before use. Oxidized copper substrates were obtained by permitting the acetic-acid-cleaned copper to react in air for several hours until a visible oxide film formed. Sulfided copper substrates were produced by treating copper with a stream of hydrogen sulfide at 440°C for 3 hr. This treatment converted the coupons almost completely to CuS.

A single-crystal boule of Al_2O_3 -doped rutile (grown by the Verneuil technique with a C-axis growth direction) was obtained from the National Lead

Company. The crystal was oriented along the $\langle 001 \rangle$ direction by back-reflection Laue techniques, and wafers approximately 2 mm thick were cut with a diamond saw. The wafers were polished with 1- μm Al_2O_3 powders. They were then either oxidized in an oxygen stream at 440°C for 3 hr or reduced in a hydrogen stream at 440°C for 3 hr.

After cleaning, the coupons were placed in baths of buffer solutions of various pH for 5 min. They were then removed and lightly blotted without rinsing. Lead naphthenate was applied by pipetting a small quantity of the heptane solutions (approximately 2 μl) onto the surface and permitting it to dry. This produced three to ten monolayers of lead naphthenate on the substrate. Once prepared, samples were placed into the vacuum chamber, and the chamber was evacuated within a few minutes.

Several standard compounds were also analyzed. Lead foil was examined before and after argon ion sputtering. Lead oxide, lead nitrate, lead acetate, and lead cyclohexanecarboxylate powders were mounted in the spectrometer by applying them to double-stick tape on aluminum coupons. Lead dioxide was formed by anodic deposition from an aqueous $\text{Pb}(\text{NO}_3)_2$ solution onto a platinum electrode.¹ Saturated solutions of Pr and Dy 2, 2, 6, 6-tetramethylheptanedionates (Pr- and Dy-Resolve obtained from Alpha Ventron) in heptane were applied to steel substrates by the same methods as used for lead naphthenate. These two compounds are not lubricant additives but were chosen as standards with which to compare certain trends in the lead naphthenate adsorption results.

All binding energies were corrected to a carbon 1s binding energy of 285.0 eV to compensate for the effects of sample charging. The precision with which binding energy can be determined is ± 0.2 eV. The relative

abundance ratios reported are determined from the intensity of the specified XPS peak (after any necessary deconvolution, which was done by hand), corrected for the tabulated differences in sensitivity of the spectrometer for the various elements. Intensities can be measured with a precision of 10 to 20%.

RESULTS

The XPS results obtained from the standard samples are listed in Table I. Also listed are literature values of the $Pb(4f_{7/2})$ binding energy for several of the compounds. In all cases where a comparison is possible, the values determined in this work are compatible with the literature values. Lead compounds are one of the few classes of compounds in which the binding energy of the lead core electrons does not increase monotonically with the increase in the formal oxidation state of the lead atom. This is evident from the data in Table I: the $4f_{7/2}$ binding energy of $Pb(0)$ is 136.8 eV, that of $Pb(II)$ in PbO is about 138.2 eV, whereas that of $Pb(IV)$ is 137.5 eV. Explanations of this behavior have been advanced elsewhere.^{2,3}

The binding energy of the $Pb(4f_{7/2})$ electrons in lead naphthenate measured 139.1 ± 0.2 eV. This value is similar to that measured for lead acetate and lead cyclohexanebutyrate, which are also $Pb(II)$ compounds. It is higher than that of PbO , reflecting the importance of substituent effects in determining the binding energy. The binding energy of the $Pb(4f_{7/2})$ electrons of PbO is approximately 1 eV lower than that of oxidized lead foil. This is a general phenomenon in the oxidation of metals.⁴ Bulk oxides usually have lower electron binding energies than the corresponding oxidized metal, possibly because of the differing coordination and bond strengths of surface compounds compared with bulk materials.

In these experiments, the XPS spectra of lead naphthenate adsorbed on any of the substrates were quite similar in overall features (Fig. 1). In all cases, lead with a $4f_{7/2}$ binding energy of about 139 eV was present.

Table I. Binding energy of Pb(4f_{7/2}) electrons

Material	Binding energy (eV)	Reference
Pb, before sputtering	139.2	a
Pb, after sputtering	138.1, 136.8	a
	136.9	b
	136.6	c
PbO	138.2	a
	137.9	b
	138.2	d
Pb(NO ₃) ₂	139.3	a
Pb(CH ₃ COO) ₂	138.7	a
Pb(C ₆ H ₁₁ (CH ₂) ₃ COO) ₂	139.2	a
Pb(CH ₃ COO) ₄	137.4	a
PbO ₂	137.6	a
	137.5	b
	137.6	d

^aThis work.

^bK. S. Kim, J. J. O'Leary, and N. Winograd, Anal. Chem. 45, 2214 (1973).

^cR. B. Shalvay, G. B. Fisher, and P. J. Stiles, Phys. Rev. B 15, 1680 (1977).

^dJ. M. Thomas and M. J. Tricker, J. Chem. Soc. Faraday Trans. II 71, 329 (1975).

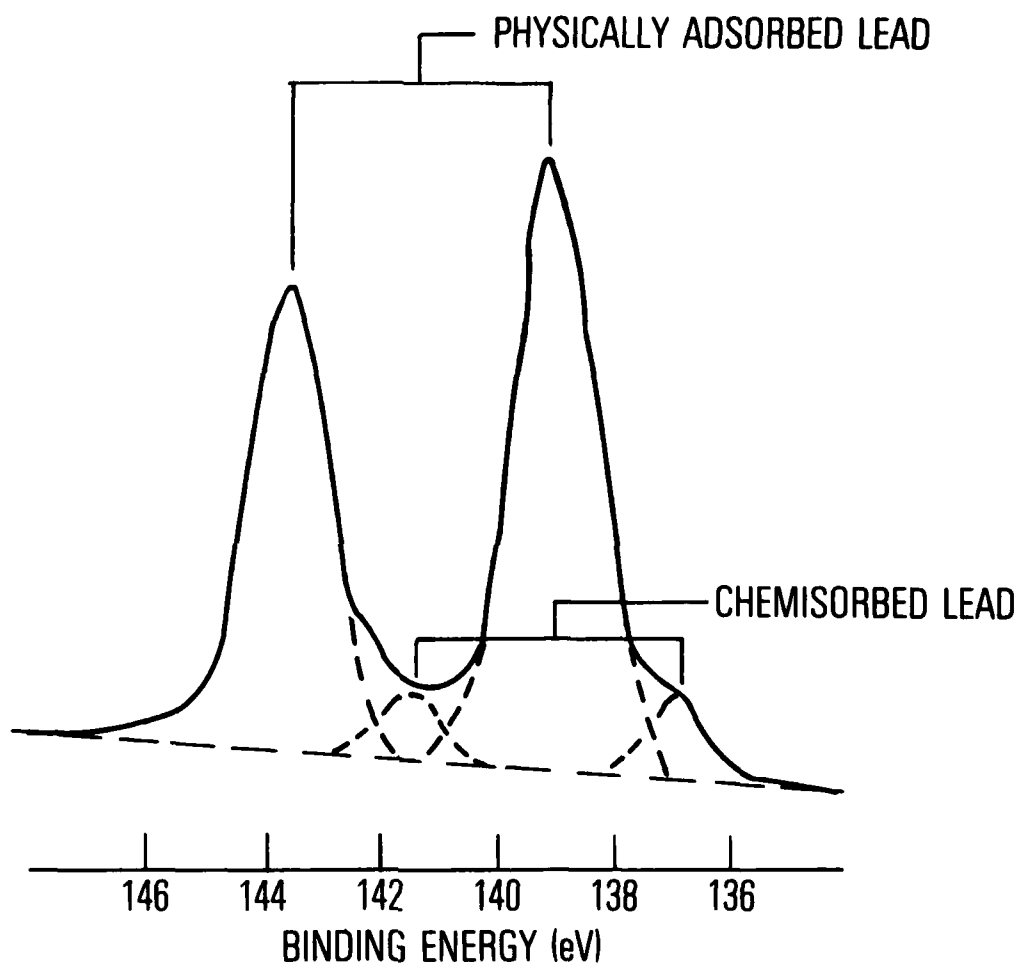


Fig. 1. Pb(4f) region of XPS spectrum of lead naphthenate on 304 stainless steel pretreated in pH 5 solution.

This value is the same Pb binding energy as was found in pure lead naphthenate and is taken to indicate the presence on the surface of lead naphthenate that is undisturbed by the surface. It was present on all substrates for all pretreatments and could be physically adsorbed lead naphthenate or a bulk overlayer of lead naphthenate.

In addition to the physically adsorbed lead naphthenate, a second form of lead was present on the surface in many cases. Under certain conditions, a second set of Pb(4f) XPS peaks was observed in the spectra at a lower binding energy than the aforementioned lead naphthenate peaks. A typical spectrum is shown in Fig. 1. The binding energy of the Pb(4f_{7/2}) electrons is approximately 136.6 eV for this second form of lead, when it occurs, regardless of the substrate. Because of the lower binding energy of this state of lead naphthenate, it probably corresponds to a reduced form of lead with a stronger, chemisorptive interaction with the surface. The Pb(4f_{5/2}) peak behaves similarly to the Pb(4f_{7/2}) peak.

The existence of the second binding state is very dependent on the surface conditions, particularly on surface acidity. The influence of the pH of the pretreatment bath used for the substrate on the existence of chemisorbed lead naphthenate is shown in Fig. 2. In this case, the substrate is gold. After acidic baths, only one form of lead is present on the surface, physically adsorbed lead naphthenate. However, after an alkaline pretreatment bath, physically adsorbed and chemisorbed lead naphthenate are found.

As evident in Fig. 2, the transition between a surface with only physically adsorbed lead naphthenate and one with both states is very sharp. The pH at which the chemisorbed state appears is dependent upon the substrate.

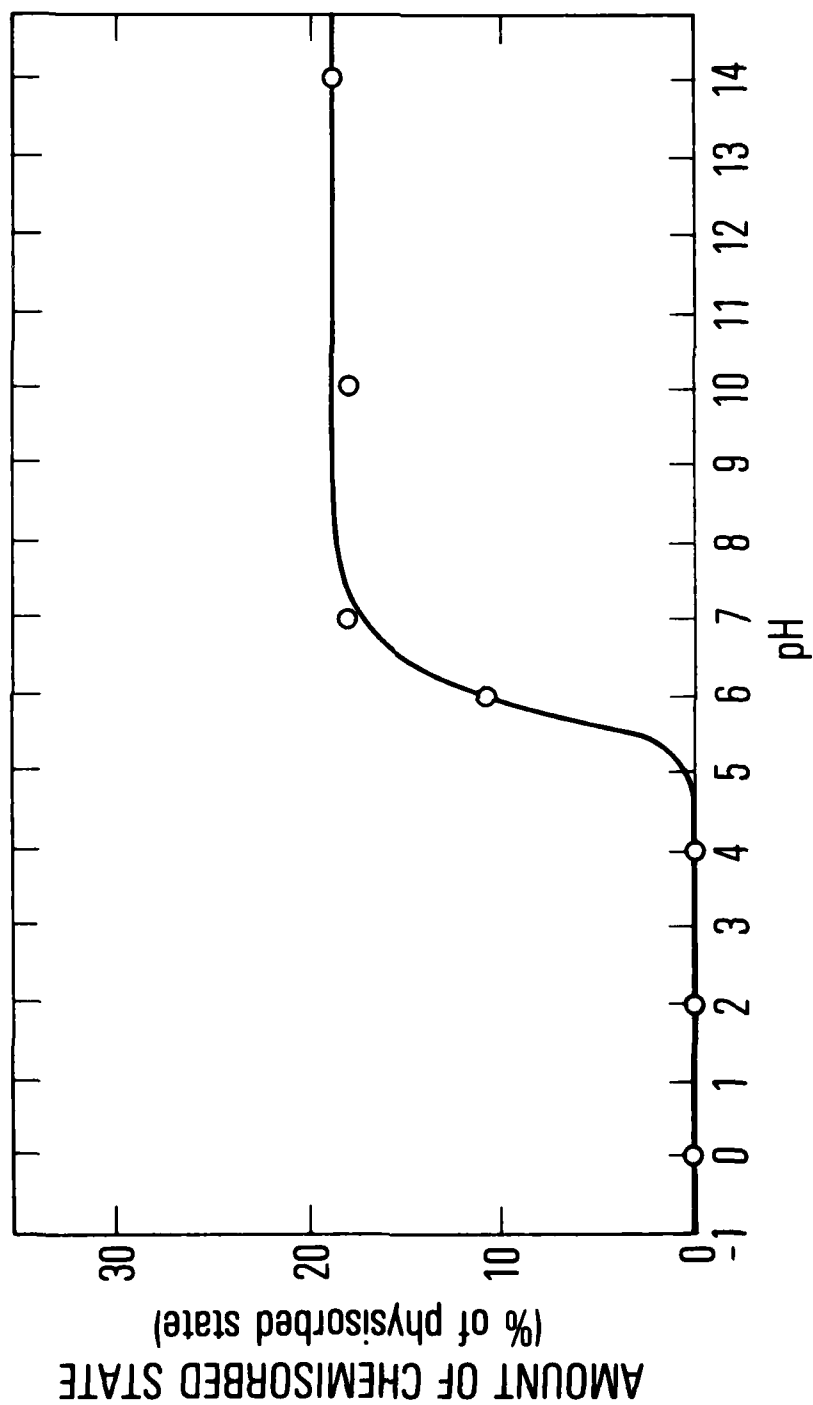


Fig. 2. Amount of chemisorbed lead naphthenate with respect to the physically adsorbed state vs pH for a gold surface. The relative amount of lead is calculated from $Pb(4f_{7/2})$ peak intensities.

For gold, this pH is 6, whereas for steel it is 2, and for nylon it is about 0.5. Values of transition pH for several other surfaces are included in Table II. The pH of transition is determined from the experimental data with a precision of ± 1 pH unit. Similar sharp transitions as a function of pH have been reported for the adsorption isotherms of transition metal ions on SiO_2 and TiO_2 powders.⁵

The results for TiO_2 (rutile) crystals are presented in Fig. 3. Rutile is the form of the oxide layer that forms on titanium metal surfaces under normal atmospheric exposure. The differences in transition pH between the oxidized and reduced crystals clearly indicate the influence of surface composition on the formation of chemisorbed lead naphthenate. There are two forms of oxygen on TiO_2 surfaces, one with a binding energy of 529.9 ± 0.3 eV and another with 532.3 ± 0.2 eV. The relative amounts of these two oxygen states are dependent on the pretreatment of the surface. For reduced TiO_{2-x} , the high binding energy peak becomes more important as the pH of the pretreatment bath increases (Table III). Even before pretreatment in the baths, oxidized TiO_2 has more of the 532.3 eV oxygen than reduced TiO_2 .⁶ The surface oxygen atoms, especially those with a binding energy of 532.3 eV, seem to have a large effect on the surface bonding of lead naphthenate.

The influence of surface composition is also illustrated in Fig. 4, where the surface of clean copper is seen to behave like that of gold, with a transition pH of 6. Oxidized copper has a much lower transition pH (≈ 1), reflecting the presence of surface oxygens as in the case of oxidized TiO_2 . Similar behavior was found for the sulfided copper coupons: the sulfur atoms apparently perform the same function with respect to chemisorbed lead naphthenate as do the surface oxygen atoms on oxidized copper.

Table II. Values of pH at which chemisorbed Pb is formed

Material	pH
Gold	6
Steel (440C or 304)	2
Nylon 66 ^a	0.5
Kapton ^b	0.5
Teflon FEP ^c	0.5
TiO ₂ (oxidized)	1.5
TiO ₂ (reduced)	7
Copper (clean)	6
Copper (oxidized)	1
Copper (sulfided)	3

^aPolyamide

^bPolyimide

^cFluorinated ethylene propylene

Table III. Ratio of intensity of 532.3-eV to 529.9-eV oxygen signals for TiO_{2-x}

pH	Intensity ratio
-1	0.60
2	0.83
4	1.3
6	1.1
8	1.4
10	1.7
13	2.3

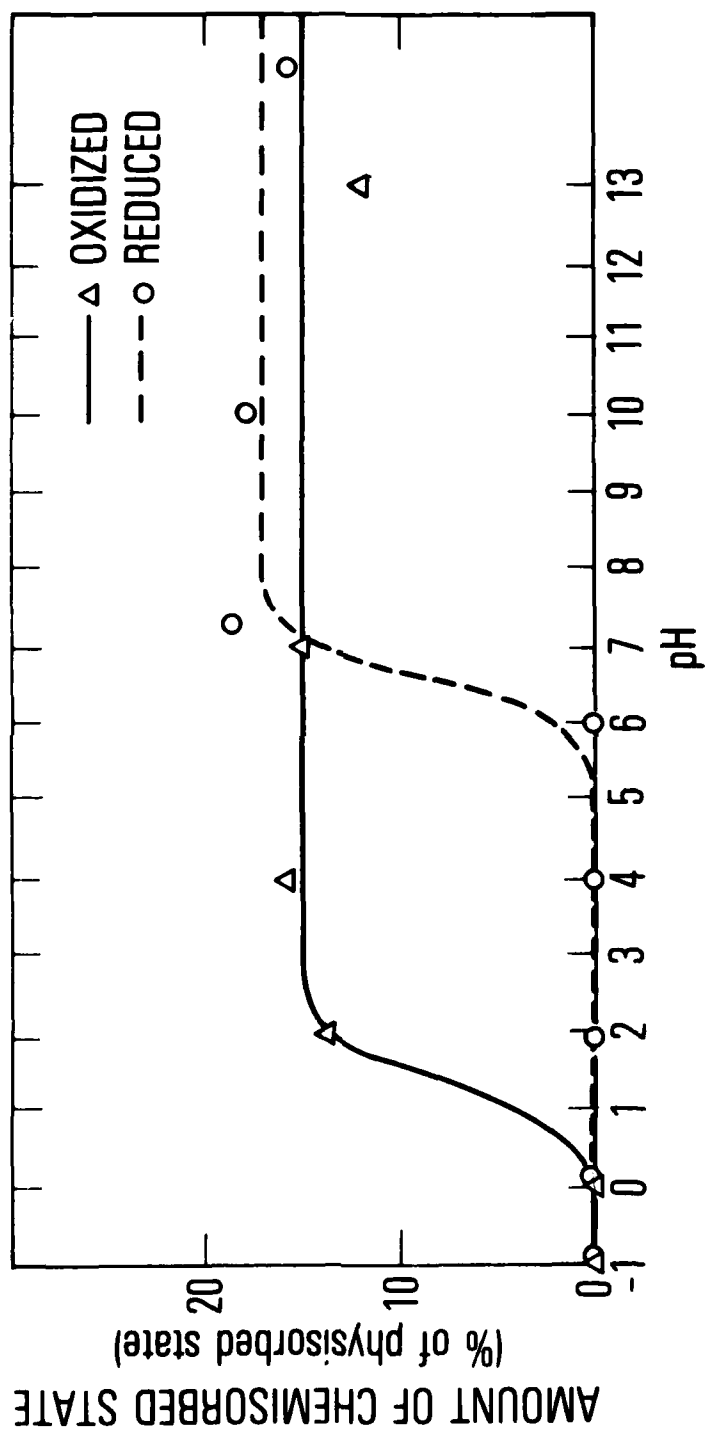


Fig. 3. Amount of chemisorbed lead naphthenate with respect to the physically adsorbed state vs pH for TiO_2 crystal surfaces, calculated as in Fig. 2.

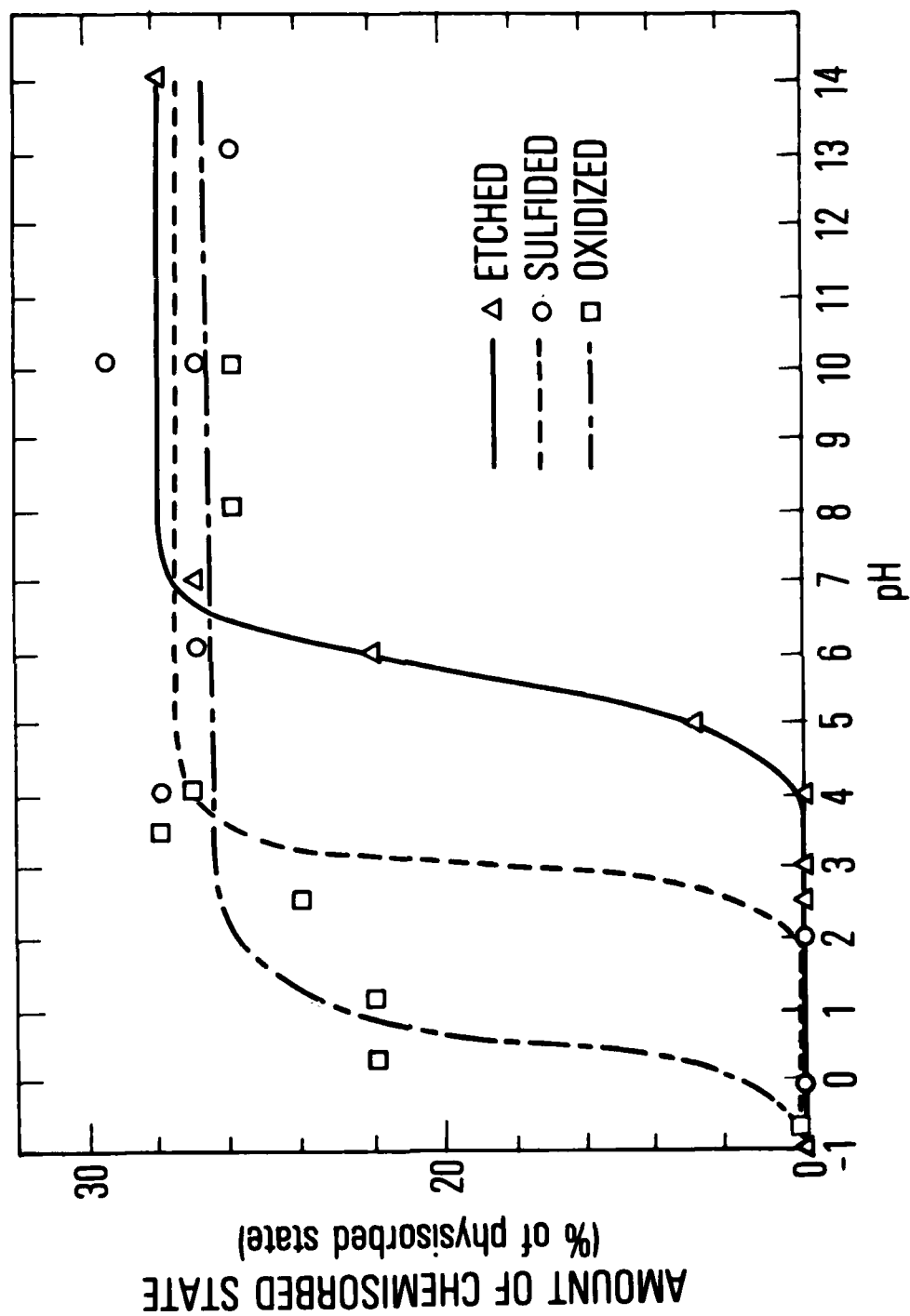


Fig. 4. Amount of chemisorbed lead naphthenate with respect to the physically adsorbed state vs pH for Cu surfaces, calculated as in Fig. 2.

In addition, for the sulfided copper samples, the sulfur 2p peak exhibits an interesting behavior. After a low pH bath [Fig. 5(a)], only physically adsorbed lead naphthenate is present on the surface, and only one form of sulfur is present. This sulfur, with a 2p binding energy of 162.4 eV, is the sulfur in CuS. After a high pH bath [Fig. 5(b)], both physically adsorbed and chemisorbed lead naphthenate are on the surface, and two forms of sulfur are present. One is CuS, as before, with a binding energy of 162.4 eV. The other has a higher binding energy, 167.8 eV, which indicates a more oxidized, electron-deficient form of sulfur than that in CuS. Binding energies are reported as 160.5 eV for PbS, 164.0 eV for elemental sulfur, and 166 to 169 eV for various sulfites and sulfates.⁴ Thus, the sulfur with a binding energy of 167.8 eV is much more electron deficient than a sulfide or elemental sulfur and has an electron density similar to a sulfite or sulfate. For all sulfided copper samples, if there are two forms of lead there are also two forms of sulfur. Unlike the TiO₂ surface, on which there are two types of oxygen before adsorption of lead naphthenate, on CuS, after pretreatment but before lead naphthenate adsorption, there is only one kind of sulfur. An additional high binding energy peak might be expected in the oxygen signals for other samples such as oxidized copper, but the oxygen spectra are broad, consisting of several peaks as a result of different oxygen species (e.g., carbonates, oxides, and hydroxides) and cannot be deconvoluted uniquely.

The behavior of adsorbed praseodymium and dysprosium tetramethylheptanedionates is similar to that of lead naphthenate. However, instead of

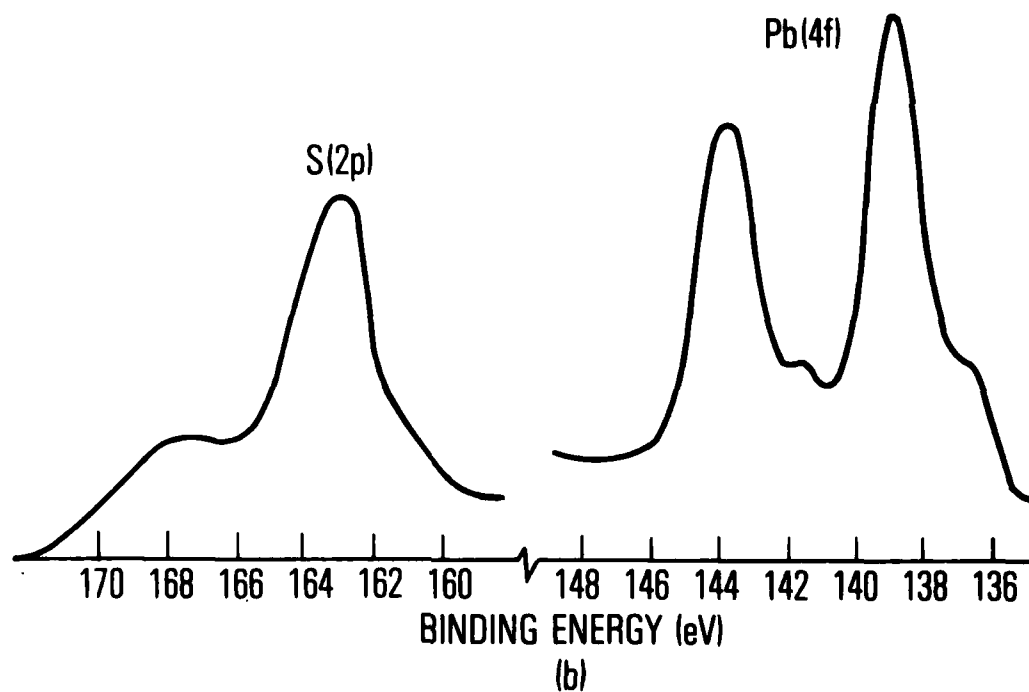
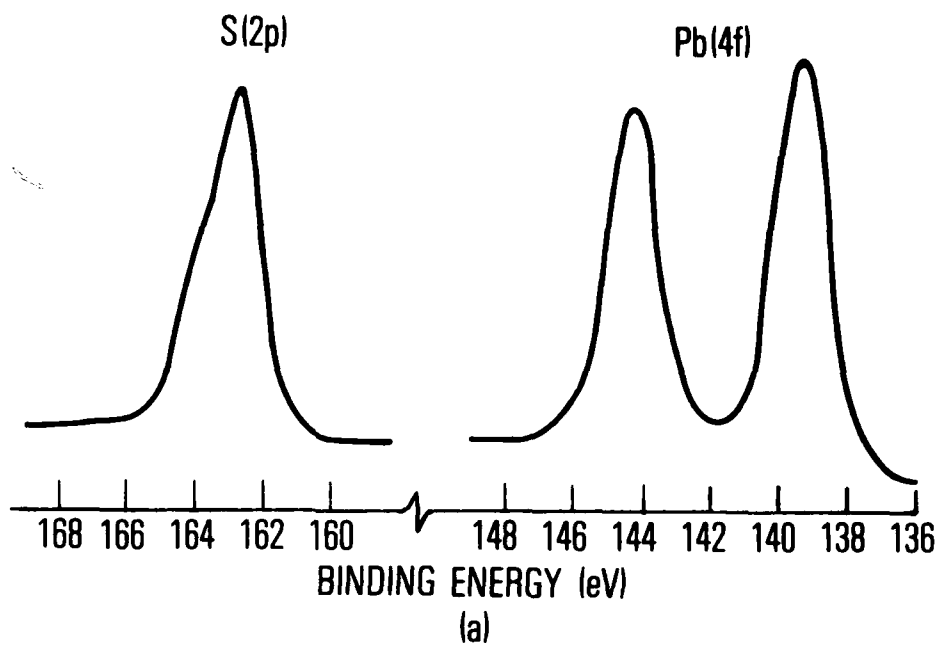


Fig 5. S(2p) and Pb(4f) regions of XPS spectrum of lead naphthenate on CuS: (a) surface pretreated in pH -1 solution, (b) surface pretreated in pH 10 solutions.

an abrupt transition from only one set of XPS peaks to two sets, as for lead, for the rare earths there is a smooth change in binding energy from higher energy on acidic surfaces to lower energy on basic surfaces (Table IV).

Table IV. Pr- and Dy-(C₁₁H₁₉O₂)₃ on 304 steel

Material	pH	Binding energy (eV)
Pr(C ₁₁ H ₁₉ O ₂) ₃ ,	-1	934.0
Pr(3d _{5/2}) peak	2	933.8
	8	933.3
Dy(C ₁₁ H ₁₉ O ₂) ₃ ,	-1	157.9
Dy(4d) peak	2	157.8
	6	157.4
	13	157.3

DISCUSSION

Lead naphthenate adsorbs on surfaces in two possible forms, which can be distinguished by their distinct XPS spectra. One form is always present and has a $\text{Pb}(4f_{7/2})$ binding energy identical to that of bulk lead naphthenate. This bonding state has been identified as physically adsorbed lead naphthenate or a bulk overlayer of the material, since no strong lead-surface interaction is present to disturb the lead core electrons.

A second bonding state, one in which there is a strong lead-surface interaction, is also possible. The interaction is responsible for lowering the $\text{Pb}(4f_{7/2})$ binding energy by 2.5 eV, relative to physically adsorbed lead naphthenate, and is associated with the presence of basic sites on the substrate surface. The importance of basic sites is clearly evident from the results for gold and clean copper: only physically adsorbed lead naphthenate is present unless the substrate has been treated in a basic bath.

The oxygen and sulfur anions present on the surface of oxidized and sulfided copper, respectively, also provide basic sites for lead naphthenate chemisorption. Pretreatment of the surface in a bath of pH 6 or greater is not necessary in order to produce the lower binding energy form of adsorbed lead naphthenate, since these basic sites are already available to the lead naphthenate.

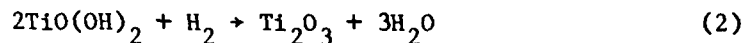
The same effect is observed on TiO_2 . The surfaces of TiO_2 have at least two different kinds of oxygen or hydroxyl groups as indicated by both XPS and infrared spectroscopy.⁷ These different hydroxyls can be categorized

as terminal or bridged, depending on whether the oxygen is bonded to one or more titanium ions, respectively. For the 001 face of rutile, there are geminal pairs of terminal hydroxyls (i.e., two OH bonded to a single titanium ion and extending outward from the surface) and bridged hydroxyls where the oxygens are bonded to two titanium ions, one in the same atomic plane and one a one-half unit cell thickness below the surface plane. Fully oxidized surfaces have a higher concentration of hydroxyls than do reduced surfaces. The presence of these extra hydroxyls apparently has a significant influence on the bonding of lead naphthenate to the TiO_2 surface, since oxidized TiO_2 requires a much less basic pretreatment than does reduced TiO_2 to produce the chemisorbed lead naphthenate.

The relatively high transition pH values for gold, reduced TiO_2 , and etched copper reflect the difficulty and necessity of bonding OH groups to these surfaces as precursors to the formation of the chemisorbed lead naphthenate species. For reduced TiO_{2-x} , we speculate that it is the terminal hydroxyls that are removed during heating. Standard dehydration of the surface (i.e., heating to $>400^\circ\text{C}$ in a vacuum) removes one-half of the terminal hydroxyls, as shown in the following reaction.



Such a dehydroxylated surface is easily rehydrated.⁷ Conversely, reduction of the surface (with H_2) has the net effect of removing more than one-half of the terminal hydroxyls, as shown in Reaction (2).



The use of Ti_2O_3 does not imply recrystallization of the surface, but rather it simply represents the stoichiometry of the overall process. The surface probably consists of a small percentage of Ti^{3+} ions interspersed among the Ti^{4+} of the rutile lattice; not enough Ti^{3+} is formed to be detected by XPS. Hydration of this reduced surface probably occurs by the addition of water molecules without dissociation or surface oxidation and not by the formation of surface hydroxyls as in the case of the dehydrated TiO_2 . In any case, the reduced stoichiometry means fewer surface oxygens and accounts for the necessity to treat the surface with basic solutions before chemisorption of lead naphthenate is possible.

The XPS results for TiO_{2-x} surfaces without lead naphthenate indicate that the concentration of hydroxyl groups with high XPS binding energies (532.2 eV) increases dramatically relative to that of OH with low binding energy (529.9 eV) when the surface is treated with buffers of successively higher pH. We interpret this to mean that the high-binding-energy hydroxyl is a terminal OH, whereas the low-binding-energy hydroxyl is bridged. The concentration of bridged OH groups is relatively constant as a surface is treated with successively higher pH solutions, but terminal groups are added to coordinatively unsaturated surface titanium ions. These terminal groups are seen to be very important to the chemisorption of lead naphthenate.

The identification of chemisorbed lead naphthenate as containing either an electron-rich or electron-deficient lead compared to the physically adsorbed molecule is complicated by the behavior of lead binding energies for

different lead compounds. Both Pb(0) and Pb(IV) have lower binding energies than Pb(II), making arguments based solely on binding energy data subject to question. In these experiments, however, corroborating evidence supports the hypothesis that the chemisorbed lead naphthenate is electron rich.

First, the chemisorbed lead naphthenate is associated with basic sites on the surface. This is clearly illustrated by the dependence of the existence of the chemisorbed state on the pH of the bath in which the surface is treated. Basic sites are electron donors, and, as such, should produce an electron-rich chemisorbed lead naphthenate.

Second, the results for the rare earth solutions support the electron-rich lead hypothesis. Praseodymium and dysprosium exhibit a constant increase in binding energy with increase in oxidation state. On basic surfaces, the Pr and Dy binding energies were lower than on acidic surfaces, clearly indicating electron-rich metal atoms on the basic surfaces. It is reasonable to expect that the tetramethylheptanedionates are subject to similar surface interactions as the naphthenate; thus, by analogy to the Pr and Dy compounds, the lead in lead naphthenate is electron rich in the chemisorbed state.

Third, XPS results indicate a relatively electron-poor surface component in at least one case: that of sulfided copper. If the sulfur atoms are donating electrons to lead naphthenate, in addition to electron-rich lead, one would expect to find electron-poor sulfur. This is just what is observed. The second sulfur peak in the XPS spectrum, which appears concurrently with the chemisorbed lead, has a higher binding energy than the CuS sulfur.

Since sulfur binding energies increase monotonically with increasing oxidation state,⁴ electron-poor sulfur is clearly indicated. The binding energy of the electron-poor sulfur is higher than that of sulfides and elemental sulfur, but is within the range of binding energies of sulfites and sulfates. We believe that the electron-poor sulfur observed in our experiments is not the result of the formation of these compounds but, rather, the result of electron donation from sulfur to lead. On surfaces without lead naphthenate, the electron-poor form of sulfur is not present, clearly indicating that lead naphthenate is necessary for its formation. Electron-poor oxygen atoms are expected on those surfaces for which they are the electron-donating group, but the oxygen spectra obtained are too complex for convincing deconvolution.

In conclusion, lead naphthenate can adsorb either physically or chemically on surfaces. The physically adsorbed state is always present when the molecule is deposited on a surface. The chemisorbed state, in which the surface donates electrons to lead naphthenate, is present only on surfaces with basic sites, such as metals that have been treated in base, or oxides and sulfides. If the general belief that chemisorption is necessary for good boundary lubrication is true, these results help to explain the efficacy of lead naphthenate as a boundary lubricant.

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